Ozone Generation Using Micro Barrier Discharge in Water

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An ozonizer operating in water for the generation of ozone water was proposed and examined. The key to ozone generation was the use of a flat circular Shirasu porous glass (SPG) with a mean pore diameter of 10μm, which functioned in bubble supply and the formation of micro-barrier discharges. The micro-barrier discharges were formed in micropores of the SPG, and bubbles formed in contact with the SPG surface facing the water phase side. The higher the applied ac voltage, the higher the uniformity of discharges and ozone concentration became. In the case of a SPG membrane with a mean pore diameter of 10μm, we confirmed that an optimal gas pressure existed at around 120kPa.

Keywords: ozonizer, water purification, bubble, ozone concentration, barrier discharge,

1. Introduction

The areas of ozone applications such as disinfections, deodorization, and water purification are expanding, rapidly [1-3]. In the field of the water purification, for example, the system application doesn't progress as much as expected so far because further equipment investment in the place of chlorination is required. To popularize the water purification using ozone widely, a low-cost with high efficiency purification system is desired. One of effective technique which may solve the problem is the generation of discharge in water, which can supply not only ozone but also atomic oxygen, OH and other radicals can be utilized for the water purification.

In this study, we proposed a novel technique for the generation of ozone in water. The key to ozone generation in water is the use of a Shirasu porous glass (SPG) [4-5] membrane obtained from SPG Technology, which plays roles in bubble supply and the formation of micro-discharges in water. The ozonizer consisted of the SPG and a mesh electrode arranged on the SPG. Applying ac voltage to the mesh electrode facing gaseous phase side, micro-barrier discharges were generated in micropores of the SPG and bubbles in contact with the SPG surface facing water phase side. Ozone and other radicals generated directly by the discharges can promote water purification. The ozone generation was examined under various conditions. Based on the results, we discussed desirable discharge conditions.

2. Experimental methods

Figure 1 shows the structure of proposed ozonizer using a SPG membrane with a mean pore diameter of 10 μm, a thickness of about 0.7 mm and a diameter of about 20 mm. Oxygen was introduced from the upper side of a cylindrical vessel 140 mm in height and 35 mm in diameter. A mesh electrode with a mesh size of 50 μm was arranged on the SPG surface facing the gaseous phase side. On the mesh electrode, a cylindrical copper electrode which made the connection between an ac power source and a mesh electrode easy was arranged. The diameter of the mesh electrode was 24 mm while that of the SPG was 20 mm. Therefore, the surface area of the mesh electrode, which was larger than the SPG, was covered with insulating adhesives. Figure 2 shows images of the surface and the cross section of a SPG with a mean pore diameter of 10 μm, obtained by scanning electron microscopy (SEM). It may be seen from this figure that pores with a diameter of 10 μm distribute uniformly.

Figure 3 shows a schematic diagram of our experimental equipment. Purified water (300 ml) with water temperature of 296 K was poured into a cylindrical glass vessel 90 mm in diameter and 115 mm in height. Our proposed ozonizer shown in Fig. 1 was arranged in the glass vessel. The distance from the bottom of the vessel to the SPG surface was about 15mm and that from the SPG surface to the surface of water was about 45 mm. Oxygen (O_2) was introduced into the outside of the SPG membrane and forced through the SPG pores at a transmembrane pressure larger than the bubble point pressure, by which bubbles were generated from the pore opening. The generation of bubble in water was confirmed at 118kPa for the case of a SPG with a mean pore diameter of 10 μm. Although the mean pore diameter was 10 μm, bubbles

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combined among themselves and the bubble diameter became several mm even at the surface of the SPG. In this experiments, the gas pressure of O_2 was set at 118, 119, 120, 121, and 122 kPa. Oxygen flow rate (Q) was around 14 l/min.

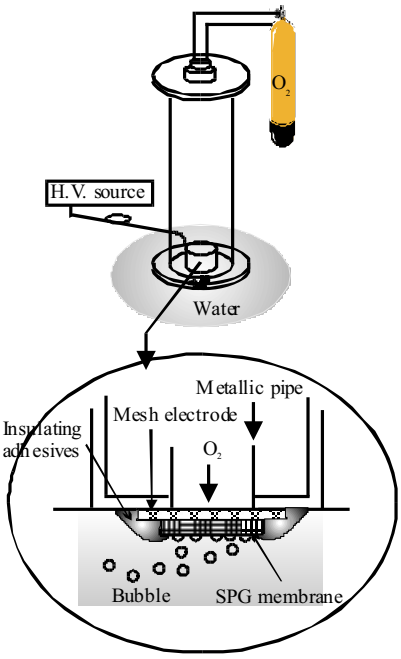

Fig. 1 Structure of proposed ozonizer.

(a)

(b)

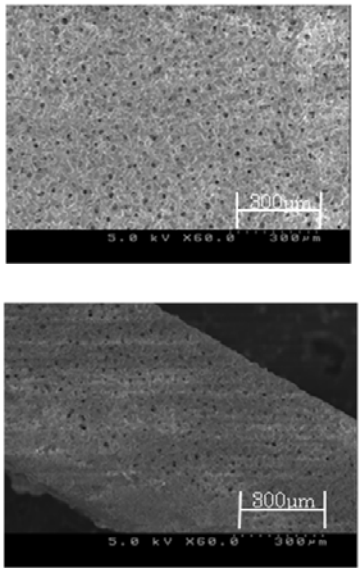

Fig. 2 SEM images of (a) the surface and (b) the cross section of SPG membrane.

To generate micro-barrier discharges in micropores of a SPG and bubbles in contact with the SPG surface facing the water phase side, an ac voltage within several kV with a frequency of 6 kHz was applied to a mesh electrode. Discharge voltage and discharge current were monitored using a high-voltage probe and a Rogowski coil, respectively. The concentration of ozone passed through purified water was measured using an ozone monitor for 600 s.

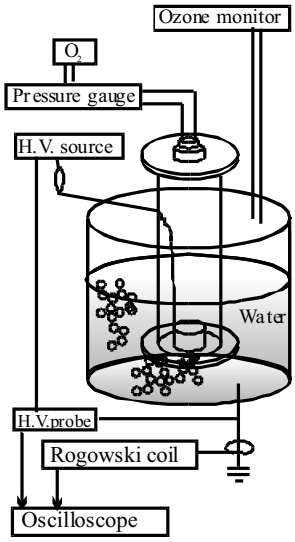

Fig. 3 Schematic diagram of experimental equipment.

3. Results and discussions

Figure 4 shows a typical photograph of the surface of a SPG facing the water phase side, taken through water and the vessel wall. The voltage applied to a mesh electrode and the operating gas pressure was 2 kV and 120 kPa, respectively. The center of the photograph indicated by a white dotted circle denotes discharges in bubbles generated in contact with the SPG surface facing the water phase side. The optical emission due to the discharges was confirmed even at 1.4 kV, and the intensity increased with an increase in applied voltage.

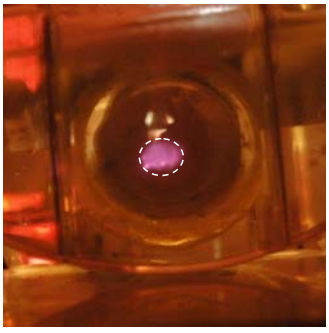

Fig. 4 Photograph of micro-barrier discharges.

Figures 5, 6, 7, 8, and 9 show variations in ozone concentrations at 118, 119, 120, 121, and 122 kPa. It can be seen that variations of ozone concentrations with the time elapsed after the voltage application for the cases of 120, 121, 122 kPa are the almost same, and their ozone concentrations after 60 s are almost steady. The ozone concentration increases with an increase of applied voltage. Except the results obtained at 118 kPa, the lower the pressure, the higher the ozone concentration becomes. Q increased with an increase of gas pressure in our experiments. The ratio of O_2 molecules which were nonliable to chemical reaction to form ozone through micro-barrier discharge increased with the increase in O_2.

The applied gas pressures of 118 and 119 kPa were the almost same at the bubble point pressure; therefore, the permeation of water through a SPG membrane easily occurred at such pressures. The discharge voltage became unsteady by the influence of the permeation of water. Such unsteady condition might cause the unsteady variation of ozone concentration. Especially, at the gas pressure of 118 kPa with the applied voltage of 1.8 kV, an intensive discharge like an arc discharge occurred and the number of micro-barrier discharges in bubbles uniformly generated in contact with the SPG surface facing the water phase side decreased. This caused the decrease of the ozone concentration. We quitted the measurement of ozone concentration when micro-barrier discharges in bubbles generated in contact with the SPG surface facing the water phase side were disappeared. A maximum applied voltage at each operating gas pressure was a critical value. An intensive discharge was generated at above the critical applied voltage whereby micro-barrier discharges in bubbles uniformly generated in contact with the SPG surface facing the water phase side were disappeared.

Under the critical applied voltage, the discharge currents were less than several tens mA, i.e., the non-equilibrium plasma was maintained. As the proof, the increase of the water temperature after the micro-barrier discharges were generated for 600 s was within 1 K (around 297 K). Micro-barrier discharge generated in micropores and bubbles is considered to be the short lived non-equilibrium plasma [6]. It is expected that the electron density and the electron temperature are around 10^{19} m^{-3} and 5 eV, respectively. However, their measurements in micropores with mean pore diameter of 10μm are difficult. Even for measurements of discharges formed on the SPG surface, they are difficult because occurrence of the discharge is closely related to frequency of bubble occurrence. We now try to investigate relationship between frequency of the bubble formation and the discharge, and then characteristics of the micro-barrier discharge will be clarified.

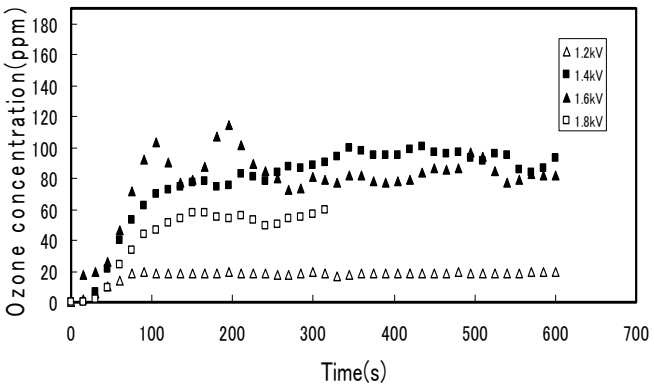

Fig. 5 Variations in ozone concentration at 118 kPa.

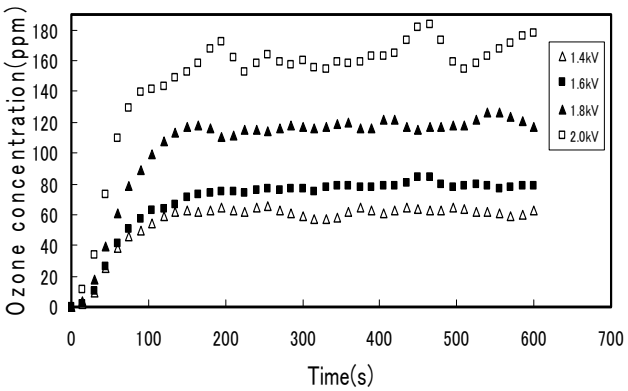

Fig. 6 Variations in ozone concentration at 119 kPa.

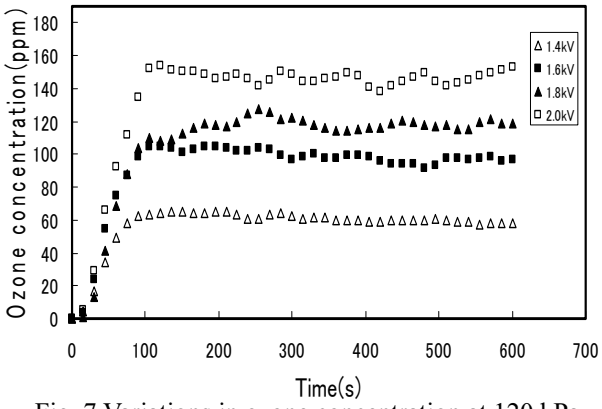

Fig. 7 Variations in ozone concentration at 120 kPa.

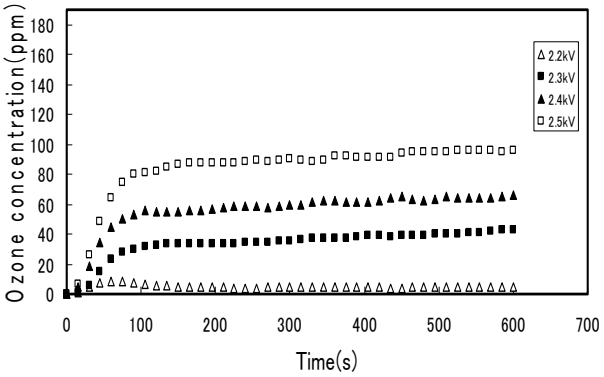

Fig. 8 Variations in ozone concentration at 121 kPa.

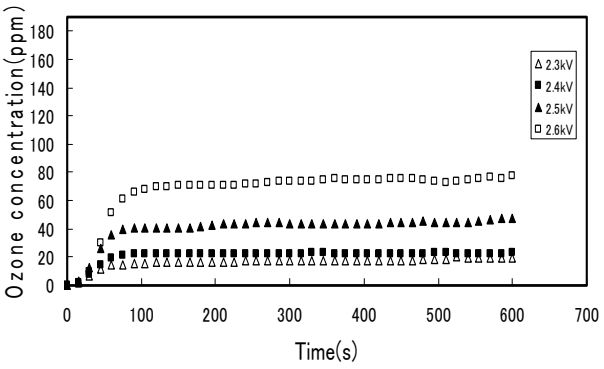

Fig. 9 Variations in ozone concentration at 122 kPa.

Figure 10 shows the variation in maximum ozone concentrations at 1.2, 1.6, and 1.8 kV. The maximum

ozone concentrations were obtained after quitting ac voltage used for generating micro-barrier discharges. The gas pressure during measurements of ozone concentrations shown in Fig. 10 was set at 122 kPa although that while generating micro-barrier discharges was set at 118 kPa. As shown in Fig. 5, maximum ozone concentrations at applied voltages of 1.2, 1.6 and 1.8 kV are 20, 118 and 60 ppm, respectively. Therefore, the ozone concentrations obtained after quitting ac voltage and setting the gas pressure at 122 kPa were higher than those shown in Fig. 5. Such phenomenon was observed only at 118 kPa. The detected ozone was considered to be remaining ones in an ozonizer. As mentioned above, the applied gas pressure of 118 kPa was the almost same as a bubble point pressure. Because the permeation of water through a SPG membrane easily occurred, ozone generated in micropores of a SPG membrane was not easily forced out from an ozonizer to water. It was considered that the remaining ozone in the ozonizer could be forced out by increasing the gas pressure.

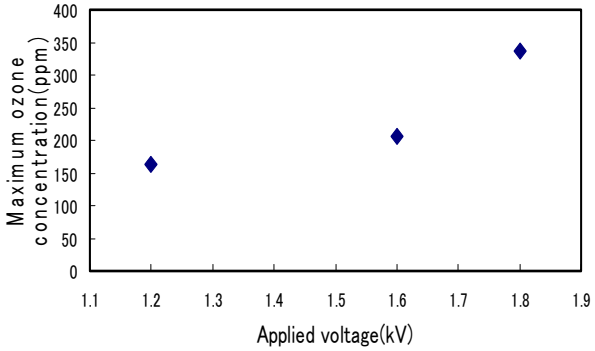

Fig. 10 Ozone concentration after quitting ac voltage and setting the gas pressure at 122kPa.

Figure 11 shows the variation in maximum ozone concentration at 1.8 kV. The ozone concentration at 118 kPa was obtained while applying ac voltage. For the cases of 121 and 122 kPa, any micro-barrier discharges were not generated and the ozone was not detected. Thus, maximum ozone concentration was obtained at 120 kPa. Variations in ozone concentrations obtained with various applied voltage and gas pressure are plotted in Fig. 12. A maximum ozone concentration was obtained at 119 kPa; however, the variation at the applied voltage of 2 kV was unstable because of the influence of the permeation of water into a SPG membrane. The ozone concentrations at 120 kPa were close to those at 119 kPa and they could be stably obtained. Therefore, we can consider that an optimal gas pressure and an applied voltage are 120 kPa and 2 kV, respectively.

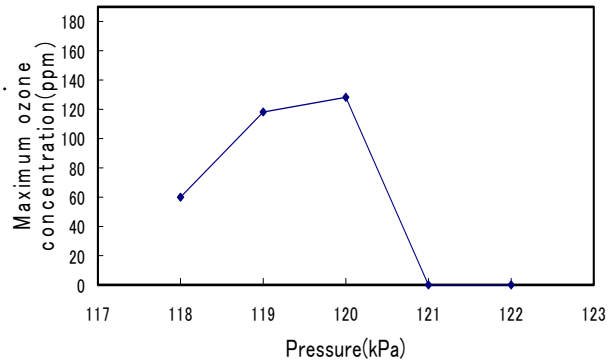

Fig. 11 Variation in maximum ozone concentration at the applied voltage of 1.8 kV.

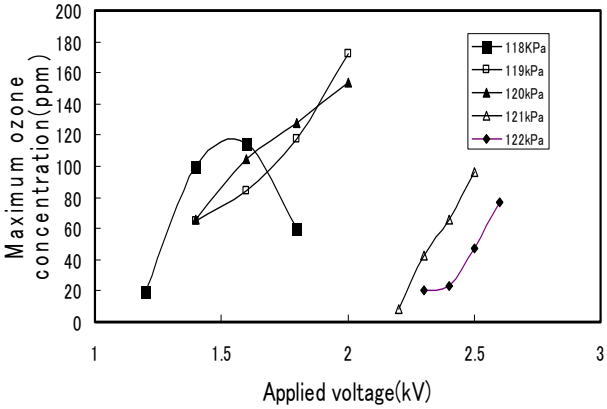

Fig. 12 Variations in ozone concentrations with various applied voltage and gas pressure.

4. Conclusions

We examined a novel ozonizer with a SPG for the generation of ozone water. Micro-barrier discharges were formed in micropores with mean pore diameter was 10μm, and bubbles formed in contact with the SPG surface facing the water phase side. The optical emission due to the discharges increased with an increase in applied voltage. The ozone concentration was monitored under various discharge conditions. The results showed that ozone was stably obtained at above 120 kPa and that an optimal gas pressure and an applied voltage existed at around 120 kPa and 2 kV, respectively.

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